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A STUDY OF THE ELECTRO-CHEMICAL CORROSION OF MAGNESIUM

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Translated from

Trudy Inst. Fiz. Khim., Akad. Nauk SSSR, 1955, 4, 172-197

by

E.R. Hope

Directorate of Scientific Information Service

DRB Canada

March, 1958

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A STUDY OF THE ELECTRO-CHEMICAL CORROSION OF MAGNESIUM

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The inferior corrosion-resistance of magnesium and magnesium alloys often seems a serious obstacle in the way of their wider use in a structural design. Therefore a thorough study of the corrosion, and of methods for protecting magnesium and its alloys, is a matter of first-line importance. Worthwhile studies in the field of magnesium alloy corrosion have been carried out, in the Soviet Union, by a number of scientists at the All-Union Machine Construction Institute for Aviation [1-4] and in the Academy of Sciences of the USSR [5,6]. The corrosion process in magnesium and in magnesium alloys is also being investigated by numerous scientists in other countries [7-8]. Nevertheless, in spite of the extensive research material which exists, there are still many obscure points involved in the mechanism of the corrosion of magnesium and its alloys.

In the present work, we have undertaken to study the mechanism of magnesium corrosion in sodium chloride solutions principally under conditions of anodic polarization of the metal.

The great interest of studying the anodic processes in particular, in the corrosion of magnesium, arises from the following circumstances.

1) Cathodic processes in the corrosion of magnesium, particularly in referred to the process of hydrogen liberation on inclusions in the metal and its alloys, may be regarded as considerably better explained [than the anodic process]. We mention, for example, the inverse relationship which V.O. Krenig and G.A. Kostylev [9] have established between the hydrogen overvoltage on cathode inclusions and the corrosive efficacy of these inclusions. This relationship holds up well in the corrosion of magnesium in electrolyte solutions.

2) The anodic processes in the corrosion of magnesium have been comparatively little studied. Here we may mention only the work of V.O. Krenig and V.K. Uspenskaya [10], who established the existence of a negative difference-effect in the corrosion of magnesium and its alloys in contact with other metals.

3) The degree of anodic control in magnesium corrosion is quite important as compared with other metals. According to N.D. Tomashov's calculations, if oxygen depolarization (corrosion in the atmosphere) is accepted as the cathode process, then anodic control in magnesium corrosion amounts to 31%, second only to anodic control in such easily passivized metals as aluminum (46%), chromium (43%) and beryllium (39%). But if similar calculations are made for magnesium corrosion under conditions of

hydrogen depolarization, which is usually the case in the corrosion of magnesium in solutions, then the figure for anodic control becomes the greater, being as much as 50%. Thus in magnesium corrosion with hydrogen depolarization, the anode and the cathode processes play approximately equal parts.

4) In consequence of the strongly negative value of the steady electrode potential of magnesium in solutions, as compared with the electrode potentials of other constructional metals and alloys, it is necessary, in all complicated designs involving different metals, to operate magnesium, and magnesium alloys also, as anodes only.

If we regard the structure of a magnesium alloy as a multiple-electrode galvanic system [11], then the anode role is always played by the basic magnesium background of the alloy structure, while the strengthening additions act as cathodic components.

5) Study of the anodic behavior of magnesium is also of great interest from the view-point of the ever-expanding use of magnesium anodes in technology, both for purposes of protective shielding and as new sources of electric current (in the electric battery industry).

6) On the scientific side, there is particular interest in the study of anode processes taking place on a magnesium electrode through the existence of the above-mentioned phenomenon of a negative difference-effect; that is, an increase in the rate of autolysis accompanying increase in the anode current density, a phenomenon which is a characteristic feature of the corrosion processes for magnesium [9,10], aluminum [12,13] and their alloys [14].

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The Research Materials

Our corrosion researches and electrochemical researches were based on a 0.5% NaCl solution. The extensive use of sodium chloride solutions for corrosion studies is due to the fact that in practice the majority of actual cases of corrosion in electrolytes have chlorine as the main corrosion-active ion. However, the use of pure NaCl solutions would not be entirely satisfactory in the present case. In the corrosion of magnesium in neutral solutions, the electrolyte pH changes markedly with time (becoming alkaline), whereas, in order to secure satisfactory reproducibility of corrosion tests and to eliminate the effect of change in the solution pH on the electrode potentials, it would be highly desirable to have the electrolyte with a constant pH.

The maintenance of a constant value of the electrolyte pH is possible if the experiments are conducted at a high rate of solution renewal, but experimentally this is very difficult; however, it is not a complete cure for inadequate reproducibility, because of the considerable pH gradient in the immediate vicinity of the electrode surface (concentration-polarization).

Therefore we decided to employ buffered solutions.

However, a buffer for corrosion experiments has to be selected with great care, since the effect of introducing the usual buffer solutions, well-known in electrochemistry, is to cause a marked change in the corrosion and to give results which it is difficult to apply to real corrosion conditions. On these grounds, we thought it most expedient to employ, for our corrosion solutions, the buffer properties of the corrosion products of magnesium itself. Given sufficiently good buffer characteristics, these solutions would, with constant electrolyte volume and a quite slow renewal rate, be entirely in accord with the conditions of actual magnesium corrosion.

Accordingly we started by investigating the pH changes in a 0.5% NaCl solution when magnesium corrodes in it. We used, for the purpose, technological magnesium, pure magnesium and, in part, ML-4 and ML-5 alloys, the chemical composition of these metals being as shown in Table 1.

TABLE 1

	Elements, in %					
	Al	Zn	Mn	Si	Fe	Mg
Pure magnesium	0.02	Traces		0.01	Traces	99.96
Technological magnesium	0.09	0.15	0.02	0.02	0.012	99.73
ML-4 alloy	6.4	2.72	0.28	-	0.05	-
ML-5 alloy	9.0	0.71	0.33	-	0.05	-

Electrodes of technological magnesium, pure magnesium, and the ML-4 and ML-5 alloys were made up in rectangular shape, 40 x 15 x 2 mm in size, with a surface area of 14 cm².

The test-pieces were cleaned with No. 000 sandpaper, degreased with 96% ethyl alcohol, dried off with filter paper, and then kept for 20 hrs in the drier over calcium chloride, so that the conditions of formation of the natural oxide film were completely identical in all cases and the state of the surface was definitely determined.

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Change of Solution pH in the Process of Magnesium Corrosion

A study was made of the process of corrosion of technological magnesium (99.7%) in an 0.5% NaCl solution. The changes of pH in the solution during the corrosion process were observed.

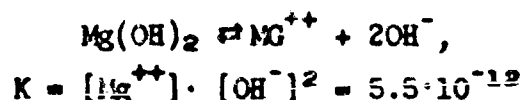
As is well known, the corrosion of magnesium in continuous immersion in chloride solutions proceeds, in most cases, with hydrogen depolarization. The only exceptions are the corrosion of magnesium in distilled water or in solutions under conditions of varying immersion, and also under conditions of corrosion in the atmosphere, where the predominant form of depolarization,

in the corrosion of magnesium and magnesium alloys, is oxygen ionization [15]. In the process of liberation of oxygen there takes place, on the cathode, an accumulation of hydroxyl ions, and the electrolyte becomes alkaline, at first on the cathodic regions and then, through diffusion or mixing, throughout the whole volume [of the electrolyte]. Thus it may be stated that the change of pH offers us a convenient means of judging the development of the magnesium corrosion process in the initial stages.

We made pH measurements both throughout the whole electrolyte volume (under conditions of mixing), using a glass ball electrode of special electrode glass, and also in the immediate vicinity of the corroding magnesium sample using a glass membrane electrode. The measurement set-up is shown in Figure 1. The emf was measured relatively to a calomel half-cell, by means of a cathode tube potentiometer. The surface area of the magnesium sample in these experiments was 14 cm². The electrolyte volume was 150 cm³.

The variation of the whole-solution pH in the corrosion process is shown in Figure 2, curve I. The pH, at first increasing rapidly, reaches a maximum in 3.5 to 4 hrs, and after that begins to decrease a little. Then, in 8-10 hrs time, a constant pH value is established, equal to 10.2 approximately.

Calculations of the pH on the basis of the known equilibrium constant K of the reaction:



gives the theoretical equilibrium value pH = 10.34 for a saturated aqueous solution of Mg(OH)₂. The maximum in curve I of Figure 2 is at a slightly higher value (10.6). This, it would seem, indicates some supersaturation of the solution with magnesium hydroxide before it begins to be precipitated out.

The final steady value of the pH (10.1-10.2) in curve I, however, is somewhat lower than the equilibrium value. This fact, in our opinion, is to be explained by a partial neutralization of the free OH⁻ by atmospheric carbon dioxide. To decide this question, pH measurements were continued after the removal of the corroding test-piece from the solution. In Figure 2, curve II, the moment of withdrawal of the test-piece from the solution is at the point marked 1; after this point, the curve goes downward (the pH decreases). Re-immersion of the test-piece (at the point marked 2) causes the curve to rise again, with the pH finally coming to the constant level 10.2. Characteristically in this case, the maximum due to the phenomenon of supersaturation of the solution is no longer observed.

This experiment fully confirms that the observed pH variation is due to some equilibrium between the rate of formation of OH⁻ ions by corrosion of the magnesium and the rate of binding of these ions. To some degree moreover, in solutions open to the air, the OH⁻ ion binding process involves, in addition to the process of Mg(OH)₂ formation, a supplementary neutralization due to the solution's absorbing CO₂ from the air.

The rising branch of the pH curve in Figure 2 corresponds to a period in which the rate of OH^- ion accumulation in the solution is greater than the rate of neutralization.

When the solubility-product of magnesium hydroxide is reached (at the very start, as we have said, there also occurs a supersaturation of the solution), an insoluble film is formed; the rate of corrosion of the magnesium declines and the rate of OH^- ion formation decreases; a situation is created in which the rate of the neutralization process becomes higher than the rate of the OH^- ion formation, and the pH falls.

Then an equilibrium will be established between the rate of the OH^- ion formation process and the rate of their neutralization, after which the pH will remain practically constant.

When we compare the time-curve of pH variation (Fig. 2) with the corrosion curve (Fig. 3) we see that corresponding to the first and second intervals on the corrosion curve there is an interval of rapid pH increase. Following this there is a decrease in the corrosion rate (the third interval), corresponding to an interval of the pH curve in which the rate of increase slows down and the pH maximum is attained. Finally, corresponding to the establishment of a constant corrosion rate there is, at first, a certain fall of the pH value and then the establishment of a constant pH. The linear part of the curve continues steadily for many tens of hours, until the dimensions of the test-piece are visibly decreased by the corrosion. The establishment of the constant corrosion rate is due to an equilibrium between processes accelerating the corrosion (film destruction, accumulation of cathodic components) and processes slowing down the corrosion rate (formation of magnesium hydroxide film).

The results of these studies have demonstrated the utility of employing, for such corrosion tests, NaCl solutions buffered by a preliminary corrosion of magnesium in them, until the pH is brought to 10.34.

Under conditions of corrosion tests in the atmosphere, and when the surface areas of the magnesium test-pieces are not very large as compared with the solution mirror, the pH will vary somewhat (10.2 to 10.1 approximately) in consequence of a certain neutralizing action by atmospheric carbon dioxide, but this slight pH variation is entirely negligible. Of course such solutions, before the experiments, should either be stored in vessels secured against penetration of atmospheric carbon dioxide, or should always be kept with corroding magnesium in them. We chose the latter procedure.

In corrosion tests in neutral solutions of metals other than magnesium, the variation of the solution pH may be less, but it will nevertheless occur. Therefore, in our opinion, it would be correct to carry out corrosion tests and electrochemical tests for a number of other metals, not just in neutral solutions of the chlorides, as has been done up to now, but in chloride solutions buffered by the corrosion products of the metal in question, corroded in the solution until a more or less stable pH value is attained, characteristic of each metal.

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Corrosion of Magnesium and its Alloys in Chloride Solutions

First we secured basic data on the nature of the corrosion processes and on the amount of corrosion in the absence of any additional external anode polarization.

The curves of corrosion rate versus time which we obtained made it possible not only to draw conclusions about the character of the corrosion process, but also to calculate quantitatively the strength of the corrosion current equivalent to the substance-rate of corrosion.

In our corrosion tests on magnesium and its alloys, both those reported in this section of our paper and those with external anode polarization reported in the other sections, we chose to employ a volumetric index of the magnesium corrosion rate (by quantity of liberated hydrogen), this decision being based on the following concepts.

1) It is well known that under conditions of immersion in chloride solutions magnesium, even when there is natural aeration of the solutions, corrodes almost purely by hydrogen depolarization (oxygen depolarization amounts to less than 1%). The exceptions (as has been established by N.D. Tomashov and T.V. Matveyeva in reference [15]) are the corrosion of magnesium in distilled water or the corrosion of magnesium under conditions of variable immersion; also in atmospheric corrosion, where the oxygen corrosion may be comparable in amount with the hydrogen corrosion, or even exceed it. Consequently, under the selected conditions (complete immersion of the magnesium in a buffered 0.5% NaCl solution), the quantity of liberated hydrogen may be taken, with adequate accuracy, as a quantitative characteristic of the magnesium corrosion rate.

2) The volumetric method is of great working convenience, and also, if one takes into account the difficulty of removing the magnesium corrosion-products without removing the metal itself (a difficulty due to the high activity of the latter), it is a method of much higher precision.

3) A major advantage of the volumetric method is the possibility of taking a whole corrosion-versus-time curve for each individual test-piece.

For each test, five parallel test-pieces were set up. Moreover, each test was carried out twice, for purposes of check.

The apparatus for the hydrogen liberation experiments was of the ordinary kind, consisting of a tank, funnel and graduated test-tube. In some of the lengthier tests a more advanced eudiometer was employed, which permitted the solution to be periodically aspirated into the burette without loss of the hydrogen liberated in the meantime (see Fig. 8).

The solution volume for each test-piece was 600 ml. The tests were conducted at a temperature of 23-25°C. The surface area and the preparation of the test-pieces were the same as in the research on the solution pH variation in the corrosion process.

The corrosion-rate study was carried out in an 0.5% solution of NaCl, previously buffered to pH 10.2 by magnesium corrosion products. In addition, separate experiments for comparison purposes were made in a non-buffered 0.5% NaCl solution. The reproducibility of the results which we obtained in the several experiments may be regarded as quite satisfactory.

A study was made of the process of corrosion development in time. The character of the corrosion at the start of the tests and during the first 10-12 hours was examined in particular detail. During this period measurements were taken every ten minutes; subsequently they were taken every hour. The curves obtained are shown in Figures 3-5.

In the curve describing the time-development of the corrosion of technological magnesium, four periods may be distinguished:

- 1) The incubation period, in which there proceeds a slow process of corrosion in pores already existing in the film; this period lasts 10-15 min. (Segments 1 and 2 of the curve are shown separately in Figure 3, on a magnified scale.)
- 2) The period of destruction of the film and acceleration of the corrosion process. The duration of this period is $\frac{1}{2}$ -2 hours.
- 3) A period in which there is a certain decrease of the corrosion rate (from the second to the third hour).
- 4) The period of establishment of a constant corrosion rate (after three hours).

This curve is in good agreement with the results on the pH variation in a 0.5% NaCl solution containing corroding magnesium, as already discussed supra.

Figure 4 is a graph showing the laws of variation in the corrosion of pure and technological magnesium in 0.5% NaCl solutions, buffered at pH 10.2 and unbuffered.

The curves permit the following conclusions to be drawn.

- 1) In buffered solutions, as one might expect, the corrosion of technological magnesium proceeds, in the initial period, at a somewhat reduced rate.
- 2) An incubation period is observed both in buffered and in unbuffered solutions. But in the buffered solutions, on account of the lower initial rate of corrosion, the maximum and constant rate is established at a much later time (after 18 hours). The curve in this case rises smoothly to the constant corrosion rate, without the characteristic bend shown by the unbuffered solutions 2-3 hours after the initiation of the corrosion process.
- 3) Pure magnesium corrodes, as indeed is to be expected, at a much lower rate than technological magnesium.

The corrosion rate at each and every moment is determined by a complicated set of different and often oppositely proceeding processes. On the one hand there are factors accelerating the corrosion process: for instance, destruction of the oxide film, the exposure of cathodic inclusions with low hydrogen overvoltages. On the other hand there are factors inhibiting the corrosion process: the formation of stable protective films of corrosion products, the crumbling off of active cathodic inclusions and their removal from the surface, the variation of the pH of the medium, and so forth.

At the moment of its immersion in the electrolyte, the magnesium is covered by a natural oxide film having pores and with breaks at the sites of cathodic inclusions. When the metal comes into contact with the electrolyte, there takes place a process of the metal's dissolving through the pores. There also takes place a process of the film's being broken down in its weaker spots by the attacking ions. Until the film is breached, we have the incubation period. As the film breaks down and metal passes into solution, new cathodic inclusions are uncovered; the total amount of cathodic areas is thus increased, and since the cathodic inclusions are much more effective than the film-cathode (the hydrogen overvoltage on them is considerably lower than on the film), it is quite clear that the rate of the corrosion process increases. In support of the above statements, we may adduce the figures for the hydrogen overvoltages on various metals in slightly alkaline solutions of 0.5% NaCl at a current density of 3 mA/cm² [10].

	<u>Volts</u>
Fe	0.485
Cu	0.67
Al	0.865
Mg, oxidized	1.845
Mg, metallic	1.855

A slow-down of the corrosion process can only be caused by formation of a film of corrosion products consisting of magnesium hydroxide or basic salts of more complex type, which are insoluble under the experimental conditions. The phenomenon of the initial inhibition of corrosion is not observed, because the corrosion products causing the inhibition are being precipitated at some distance from the electrode surface, or, in the case of the non-buffered solutions, because at the pH of 7.5-8.0 which we have at the beginning of the experiment the corrosion products are still soluble. Thus according to Britton [15] the precipitation of magnesium hydroxide takes place at a pH of about 10.

Thus when a non-buffered 0.5% NaCl solution is used, we do not have the conditions for the formation of a stable film of corrosion products capable of noticeably inhibiting the corrosion process right from the start. This means high rates of magnesium corrosion in non-buffered solutions during the initial period of action of the solution.

By the change of potential when the electrode is cleaned off, we may judge the degree of film protection provided by the magnesium corrosion products. Thus according to data in G.V. Akimov and G.B. Klark [17],

measurement of the magnesium potential after cleaning off the film, versus the potential of magnesium with the film intact, gave the following results, depending on the solution pH:

- 1) In an acid medium (0.1 n HCl), cleaning off the film produces no noticeable change of potential relative to the potential of magnesium with the oxide film.
- 2) In a neutral medium (3% NaCl) there is, when the film is cleaned off, a change of potential in the negative direction, amounting to 60-80 mV.
- 3) In the alkaline region (0.1 n NaOH) the potential changes, upon cleaning, by 300-400 mV in the negative direction.

Hence the protective properties of the film increase with increase of the solution pH in the corrosion process.

On the linear part of the curve the corrosion has a constant rate, a rate not changing with time. This period of the curve must be due to an equilibrium between the formation of a magnesium hydroxide (or magnesium carbonate) film, a process inhibiting the development of corrosion, and the destruction of the protective film, a process accelerating the corrosion.

The film destruction, with consequent uncovering of new cathodic areas, may proceed both through rupture of the film by hydrogen bubbles or through simple mechanical disintegration in the corrosion process; also by way of chemical or electrochemical breakdown (the solution process for the most part) of the film on the anodic areas, the latter being effected by the active ions of the solution (for instance, chlorine ions).

As for the corrosion of the ML-4 and ML-5 alloys, both with natural and with artificial films (Fig. 5), here the corrosion differs in character from that of pure and technological magnesium. In the corrosion of these alloys there is an incubation period of insignificant duration, after which the corrosion increases for 10-15 minutes, through film rupture; then the formation of protective layers of corrosion products, inhibiting corrosion, causes a slow-down in the rate, which after 30-40 minutes becomes practically constant.

A fact which draws our attention is that the corrosion-resistance of ML-4 and even of ML-5 is some tens of times higher than that of technological magnesium. This is not due just to the presence of manganese. For instance, a Mg-Zn alloy also is more corrosion-resistant.

Questions in connection with the higher corrosion-resistance of magnesium-manganese alloys have been investigated by V.O. Krenig, S. Ye. Pavlov, N.D. Bobovnikov [2, 4] and by a number of foreign research workers. Some theories exist re the mechanism of the effect of manganese in increasing the corrosion-resistance of a magnesium alloy, but the majority of authors explain this phenomenon by the higher resistance of a film of manganese dihydroxide $[Mn(OH)_2]$ formed in the corrosion process on a

magnesium-manganese alloy, as compared with the protective powers of the corrosion-product film on magnesium; it may also be supposed that Mn, when it enters into an alloy having iron inclusions, strongly reduces the effectiveness of these inclusions by increasing the hydrogen overvoltage on them.

The lower corrosion resistance of the ML-5 alloy as compared with ML-4 may be explained by this alloy's greater content of aluminum.

The external appearance of the test-pieces also supports the idea that the character of the corrosion is different in technological magnesium and in the ML-4 and ML-5 alloys. We encounter the most dangerous "pitting" form of corrosion in technological magnesium.

To be able to judge more fully the processes taking place in corrosion on the surface of the test-pieces, we also studied the time-variation of the potential. The curves obtained are shown in Figure 6. From the data it may be seen that the potentials of all the alloys investigated are rendered more favorable in the corrosion process. The strong improvement of the potential proceeds for 2-3 hours, after which it is gradually stabilized.

Comparison of the corrosion rate curves with the curves of the time-variation of potential show that the improvement of the potential during the first few hours of the immersion of the test-piece in the solution is connected with the parallel increase of the corrosion rate, and, consequently, is due to the predominating decrease in the cathode polarizability of the corrosion system, for instance, through exposure and accumulation of new cathodic inclusions on the surface of the alloy.

The subsequent stabilization of the potential indicates, not that the accumulation of cathodic inclusions is not prolonged without limit, but also that it is inhibited, apparently through weakening of the union of the cathodic particles with the corroding surface and their removal from the surface by hydrogen bubbles or mechanical disintegration, or through loss of electrical contact. A decrease of cathode efficiency with time may also take place through the cathodic areas becoming covered with precipitated magnesium hydroxide, as will be discussed infra.

After 2-3 hours of corrosion we get, in the majority of cases, a constant pE value, a constant rate of corrosion, and a comparatively small variation of electrode potential.

For the alloys tested under the given conditions, a more negative value of the established potential corresponds to a lower corrosion-resistance, as may be seen from the curves. The only exception is pure magnesium, which is characterized by a comparatively high corrosion-resistance at a considerable negative potential.

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Study of Magnesium Corrosion with Applied Anode Current

Here we are setting forth the principal results of our quantitative experiments on the effect of the applied anode current on the process of magnesium autolysis, which from the chemical point of view is similar to the action of a cathodic contact on magnesium.

We studied: 1) The time-variation of the autolysis with anode current of constant density, and 2) the effect of different anode current densities on the autolysis.

As our experimental material we used cast technological magnesium of 99.7% purity. The test-pieces were made in the form of discs, 32 mm in diameter and 5 mm thick. The working surface was one base of the disc, with an area of 4.52 cm².

The preparation of the test-pieces was carried out in the usual manner, as described above. The test-piece was mounted solidly in a plexiglass holder, hermetically sealed (Fig. 7). The design of the holder, as shown, guaranteed a reliable contact and hermetic sealing, and made possible, if necessary, to use the gravimetric method of determining the autolysis along with the liberated hydrogen determination; also to make measurements of the electrode potentials or polarization characteristics.

To measure the quantity of liberated gas, a burette was mounted over the test-piece (Fig. 8). As electrolyte, a 0.5% NaCl solution, buffered at pH 10.20 with corrosion products, was employed.

All the tests were carried out in a thermostat at a temperature of 25° ± 0.2°C. In all cases the cathode was platinum. The immersion of the test-pieces into the solution was effected with the current flowing. Each test was repeated not less than three times. The general agreement of the results obtained by the hydrogen determination method may be regarded as satisfactory.

The anode current was supplied by a storage battery through a circuit permitting the voltage to be regulated as necessary. This method made it possible to study the anode process while excluding the effect on it of any time-varying cathode process which would occur with contact between the magnesium and different cathode metals.

We investigated first of all the time-rate of the magnesium autolysis process at several densities of the anode polarizing current, from 0.2 to 50 mA/cm².

It was found that for all the current densities studied the autolysis rate remains constant, if the short initial induction period is ignored. Figure 9 shows graphically the results of these experiments. The relationship found for the amount of actual corrosion of the magnesium anode (autolysis, as defined by the volume of hydrogen liberated over the magnesium electrode) lines up very well with a linear time-dependence relationship for all the current densities investigated. In Table 2 we show the

steadily established autolysis rates for the magnesium anode, expressed in milliliters of hydrogen liberated over the electrode.

The data in Table 2 make evident the direct relation between anode current density and autolysis rate, for the magnesium electrode.

TABLE 2

Final Steady Autolysis Rate for Magnesium Anode (in ml of Hydrogen Liberated per cm² of Over-All Surface of Magnesium Electrode per Hour), at Different Current Densities.

Current density (mA/cm)	Autolysis rate, Mg anode ($\frac{\text{ml H}_2}{\text{cm}^2 \cdot \text{hr}}$)
0	0.022
0.2	0.044
0.5	0.33
1.0	0.53
2.0	1.04
10.0	3.65
20.0	7.30
50.0	16.80

Figure 10 is a graph of the dependence of autolysis on current density, constructed from the data in Figure 9 and Table 2. As we see, there is a linear relationship between the amount of autolysis and the density of the externally applied current over a wide range of current densities (excluding the very small densities, commensurate with the corrosion current of non-polarized magnesium). Therefore we must indubitably conclude that the application of the anode current causes an activation of the magnesium electrode, and an increase in the rate of actual corrosion proportional to the applied current density (a negative difference effect) over a wide range of current densities.

A highly interesting question is whether this acceleration of protective film destruction by the anode current is an irreversible process or, on the contrary, whether after removal of the anode current a process of renewal (healing) of the protective film will spontaneously occur, with a consequent decrease in the autolysis rate.

To answer this question, a special experiment was conducted. For a period of three hours, which corresponds to the establishment of the constant rate of hydrogen liberation, the autolysis process was observed without the anode current applied. In Figure 11, the part of the curve corresponding to this process is segment I, which indicates that after a certain deceleration, the autolysis rate becomes constant.

Then an anode current of density 0.5 mA/cm^2 was applied to the test-piece (Fig. 11a), and the process of magnesium autolysis was observed for a period of 2 hours. After application of the current, the autolysis rate increased, and soon re-established itself at a constant level. The increased rate of autolysis is shown by the steepening of the slope of segment II in Figure 11. After this, the applied current was again removed (Fig. 11b), whereupon the autolysis rate immediately began to fall and in time became constant once more (segment III), at a rate approximately equal to that which it had at the start, without the anode current applied (segment I). Thus we have to conclude that the surface of the test-piece, in the sense of its corrosion behavior, can return to its original, less active state; that is, there takes place a "healing" of the disrupted areas of the film.

The formation of the protective film after removal of the anode current consists not only in the sealing off of the active cathodic and anodic areas by the insoluble corrosion products (magnesium hydroxide) formed from the metal by secondary processes, but also may proceed by direct chemical or electrochemical interaction of magnesium with oxygen dissolved in the water, or even with the oxygen of the water.

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Study of the Character of the Local Corrosion of Magnesium with an Applied Anode Current

It is well known that magnesium, as a rule, shows a clearly expressed local type of corrosion, with formation of deep corrosion ulcers (pits). But the character of these ulcerations is strongly dependent both on the character of the metal or alloy and on the circumstances of the corrosion process (for example, the concentration of active chlorine ions).

In the present work we investigated the effect of anode current density on the character of the local corrosion of technological magnesium. We determined the cross-sectional area of the corrosion ulcers, their depth and their configuration as related to time, at constant applied current density (0.5 mA/cm^2) and, in some experiments, the effect of different current densities with equal [coulomb] quantities of electricity passed.

After exposure of the test-pieces to the corrosive bath under the proper conditions, and after removal of the corrosion products, the surfaces of the test-pieces were subjected to careful examination.

With S. Ye. Pavlov's micrometer [18], the depths of the pits were measured with a precision of up to 0.01 mm . In calculating the depths, the mean of six arbitrary measurements was taken.

The calculation of the number of pits and their cross-sectional area was handled by photographing the test-pieces with a suitable magnification, according to the sizes of the pits.

In order to obtain a high-contrast photograph with sharper definition of the boundaries of the individual pits, a paste of carbon black in grease was rubbed over the corroded surfaces of the test-pieces, which were then carefully polished.

This procedure gave the best contrasting boundaries for the corrosion ulcers and made possible a quantitative determination of the area of each ulcer by planimetry of the photographic print.

The count of the pits was made from the photographs. The areas of the individual pits were measured with the planimeter, and the total area of the local corrosion was found as the sum of the individual areas.

The measured data on the kinetics of the corrosion ulcers at a constant current density of 0.5 mA/cm^2 are set forth in Table 3. Figure 12 shows photographs of the test-pieces after anode polarization, and Figure 13 gives the curves characterizing the growth of the pits with time.

As we see, the depth of the corrosion pits increase with time according to a certain attenuating curve. With passage of time the rate of increase of depth, and also the increase in the cross-sectional area or mean diameter of the pits, becomes smaller.

It is characteristic that at constant anode current density the number of corrosion pits remains constant for quite a long time (Figs. 12 and 13, 3), and only thereafter gradually decreases. The decrease occurs because neighboring cavities come so close to each other that after a certain interval of time they merge.

For a current density of 0.5 mA/cm^2 , the process begins after 6 hours and proceeds with maximum intensity for 8 hours; after that it continues, but with reduced intensity.

As the "mean nominal area" of a pit, we take the result of dividing the total area of pitting by the original number of pits (179); that is, without taking into consideration the decrease in the number of pits through the merging which occurs in protracted periods of corrosion.

Starting from the total area of the corrosion pits and the number of pits, we calculated the area of a single pit. Taking the area of a pit as the area of a circle, we calculated the radius. Comparison of the radius thus found with the depth permits the conclusion that the depth of each pit and the radius of its cross-section in the plane of the test-piece surface have identical rates of increase.

At any given moment the depth of a corrosion pit is approximately equal to the radius of the cross-section and, consequently, the area of the pit is proportional to the square of the depth (Table 3).

TABLE 5

Growth of Corrosion Pits on the Surface of Technological Magnesium,
with an Anode Polarization Current of Density 0.5 mA/cm².

Exposure (hrs)	No. of pits per cm ²	Total area of pits (mm ² per cm ² of test-piece surface)	Mean area of individual pit (mm ²)	Mean nominal area of indi- vidual pit (mm ²)	Measured depth of pit (mm)	Calculated radius of surface of pit (mm)
2	174	3.45	0.0192	0.0192	0.081	0.078
4	179	9.49	0.053	0.053	0.161	0.130
6.5	176	14.65	0.0832	0.082	0.192	0.163
9	124	25.15	0.21	0.140	0.236	0.260
16.75	133	32.90	0.247	0.185	0.326	0.280

The equality of the radius and depth of the pit indicates an approximately uniform direction of growth of the corrosion ulcer, and permits us to assume that in general the configuration of a pit is roughly hemispherical, and the area of the pit at the test-piece surface roughly a circle (the section of a sphere along a great circle).

This nominal determination of the pit configuration is, of course, not yet adequate for any exact calculation of the area of a pit.

Even in the case that the general shape of such a pit is macroscopically close to hemispherical, the microscopic topography of its surface will, because of the crystallographic structure of the dissolving magnesium, have a strongly featured character and the surface area will not be an entirely determinable quantity.

However, if we take the degree of microtopographic roughness of the surface for a given crystallographic structure of the test-piece as approximately constant, and independent of the size of the pit, then it may be stated that the true surface of the pit will likewise increase proportionately with its cross-sectional area, or ... what amounts to the same thing ... proportionately with the diameter of the pit or its depth.

On the basis of purely geometric notions it follows, from these considerations, that the growth of a pit in depth will be proportional, at a constant autolysis rate, to the cube root of the time ($r = k\sqrt[3]{t}$), while the growth of its area will be proportional to the cube root of the square of the time ($F = k\sqrt[3]{t^2}$).

Analysis of our experimental curves for the growth of a pit in depth and cross-sectional area (Fig. 13, 1 and 2) show that to a certain degree of approximation this really is the case.

An interesting fact appears from the experimental data. The autolysis rate for magnesium (calculated from the hydrogen liberation rate) is constant in time (for a given current density), in spite of the fact that the area undergoing corrosion, within the pit, is continually increasing with time.

This interesting fact may be explained in two ways.

First, it may be supposed that the whole area inside the pit is a simultaneously active, dissolving surface. In this case there will be, with a growth of the pit proportional to the increase of its total dissolving surface, a decrease in the true anode current density, and, proportional thereto, a decrease in the autolysis rate per unit area of the active surface: that is, the decrease of autolysis resulting from decrease in the true current density will be exactly compensated by the increase in the active surface area, and thus the total autolysis rate for the test-piece will not change with time.

Second, we might suppose that the true area inside the corrosion pit is not all active surface at one and the same time. In this case we may make the likely assumption that the active dissolving surface does not depend on the total area of the pit, but is determined only by the anode current density (per unit area of the over-all surface of the magnesium anode).

It seems that the second mechanism, as previously established by the researches of N.D. Tomashov and V.N. Modestova [12] on the anodic dissolving of aluminum in chloride solutions, should be considered the more probable for the anodic dissolving of magnesium too.

It was of interest also to trace the effect of the anode current density on the character of the corrosion-pit formation process. Of course, comparison of the characteristics of pits at different anode current densities makes sense only on condition that the total amount of magnesium corroded is the same. It was with this principle as our starting-point that we carried out a series of observations, observing the character of the local corrosion on the magnesium anode after polarization with different densities of current, but decreasing the time of exposure in such a way that the product of time by current density, that is, the quantity of electricity which passed through unit area of the anode surface, remained constant. This quantity of electricity was equal to 0.0375 A-hrs per test-piece, or 0.00833 A-hrs per cm^2 of the test-piece surface, since the working surface area of the test-piece was 4.5 cm^2 .

We studied, under these conditions, the character of the corrosion pits which formed: the number of such pits per unit area of the over-all surface of the test-piece, their depth, the total cross-sectional area of pitting in the plane of the test-piece surface, the cross-sectional area of each pit, and its approximate configuration.

The procedure for determining the depth and area of the corrosion pits has been described above.

The character of the variation of local corrosion on the magnesium anode, in relation to current density, for equal quantities of electricity transmitted, is illustrated by the photographs of the test-pieces, Figure 14.

All the measurement data, demonstrating the fundamentally regular relationship between growth of corrosion pits and density of applied anode current, are given in Table 4.

TABLE 4

Character of the Corrosion Pits Formed in the Anodic Polarization of
Technological Magnesium by Current of Different Densities and Equal
Quantities of Transmitted Electricity (0.00833 A-hrs/cm²).

Current density (mA/cm ²)	Number of corrosion pits per cm ² of over-all surface area of the test-piece	Total area of corrosion pits per cm ² of test-piece surface (mm ²)	Mean area per corrosion pit (mm ²)	Mean measured depth of corrosion pits (mm)	Mean calculated radius of corrosion pits (mm)
0.1	17	13.5	0.754	0.52	0.49
0.2	33	24.0	0.723	0.45	0.46
0.5	116	42.0	0.362	0.34	0.34
1.0	181	56.0	0.310	0.24	0.31
2.0	256	66.2	0.258	0.19	0.28
20.0	889	75.0	0.084	0.09	0.16

The adduced experimental data clearly indicate the entirely definite relationship of the number of corrosion centers to the anode current density.

With increase of the current density, there is a marked increase in the number of corrosion pits, and also in their total cross-section, while, on the other hand, the depth and cross-sectional area of each individual pit decreases.

Under the conditions chosen (that is, equal amounts of transmitted electricity) the quantity of magnesium corroded off was constant. In fact, the total amount of magnesium is made up of two components: 1) the quantity of anodically dissolving magnesium, proportional to the quantity of transmitted electricity in accordance with Faraday's equivalent, and 2) the quantity of magnesium corroded through processes of anode autolysis. The latter quantity, as we have shown, is directly proportional to the current density. However, since under the conditions chosen (constant amount of transmitted electricity) the exposure time is inversely proportional to the current density, then, consequently, the total quantity of magnesium corroded by the autolysis process also remains, under these experimental conditions, constant and independent of the current density.

The increase in the number of corrosion pits which develop with increasing anode current density may be explained as follows.

The destruction of the protective film first takes place in its weaker areas. Obviously, the higher the current density, that is, the higher the positive potential applied to the anode, the greater the surface areas over which the film may be destroyed and, consequently, the greater the area in which corrosion centers may develop.

The increase in the number of corrosion centers with increasing current density will (under conditions of their approximately constant configuration and identical total amount of corrosion) of course mean a decrease in depth and area of the individual pit. The total summed area of all the pits will thus increase. The character of the corrosion becomes, one might say, more uniform with increase of the current and, on the other hand, more localized with decrease of the anode current.

Analysis of the experimental data shows that for current densities that are not too high (up to 2 mA/cm^2) the number of active points (corrosion pits) developing is approximately proportional to the logarithm of the current density (Fig. 15). Only at considerably higher current densities (of the order of $10\text{-}20 \text{ mA/cm}^2$) do active centers develop in greater numbers than would follow from this law.

It is characteristic that just as soon as corrosion centers develop the corrosion process localizes itself at these points, producing corrosion pits; as a rule, formation of new corrosion centers will then no longer take place with this anode current density.

In these experiments it was also confirmed that the calculated mean radius of the cross-section of the corrosion pit (taking its configuration as hemispherical) for fairly low current densities (up to 1 mA/cm^2 approximately) is near to the experimentally measured corrosion-pit depth (Table 4). Consequently, at these current densities a corrosion pit, once it appears, will grow in roughly equal measure both in depth and in width, thus producing a general pit-configuration close to the hemispherical.

On the other hand, at higher current densities (for instance, at 20 mA/cm^2) the cross-sectional area of the pit is approximately twice as great as its depth; that is, at large anode currents the pit will begin to increase predominantly in width. Thus at high current densities the corrosion process acquires an increasing tendency to pass from a local phenomenon into a general phenomenon, both with respect to the number of centers developing and with respect to the characteristics of their growth.

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Effect of Cathode Structural Components on the Magnesium Autolysis Process

The principal, most active cathode admixtures in technological magnesium are iron, nickel, copper and certain intermetallic compounds of these elements with magnesium [19].

It is of interest to elucidate the accelerating effect of cathodic structural components on the corrosion of magnesium in neutral chloride solutions.

To determine the operative efficacy of microcathodes on the surface of corroding magnesium, we performed the following experiment.

Copper was deposited on the surface of one magnesium test-piece from a solution of 15% CuCl + 0.8% HCl for a period of one minute; on another test-piece, for a period of 20 seconds. Thus the first test-piece had approximately three times as much deposited copper as the second. The autolysis rates for these magnesium test-pieces, in an 0.5% NaCl solution buffered with magnesium corrosion products and with anode polarization and a current density of 0.5 mA/cm², were compared with the autolysis rates of the same test-pieces under the same conditions, but without the deposits of copper. The results of the experiment are shown in Figure 16.

During the first few minutes the dissolving rate of the test-pieces with the copper were considerably higher (5 to 8 times higher, depending on the quantity of deposited copper) than the dissolving rate of the ordinary magnesium test-pieces. But thereafter, in spite of the fact that the autolysis rate remains practically constant for the ordinary magnesium test-pieces, the initial autolysis rate for the coppered test-pieces decreased greatly with passage of time, establishing itself at a constant level only after 3-4 hrs. This final steady rate of autolysis is then no longer very different from that of the ordinary magnesium test-piece with no copper on it.

With steady conditions established, the autolysis rate of coppered magnesium test-pieces is 2 to 3.2 times higher than the autolysis rate of ordinary magnesium (depending on the amount of deposited copper). From this experiment it follows that the effectiveness of cathodic particles deposited on the surface of magnesium diminishes very rapidly with time.

Evidently this happens for the following two reasons: 1) at points of active dissolving of magnesium (corrosion pits) the deposited copper is simply scaled off by mechanical disintegration and is removed from the surface; 2) on areas where there is no corrosion, the cathodic particles lose their efficacy through being covered and blocked by magnesium corrosion products.

Thus we have to conclude that under conditions of corrosion in a neutral chloride solution (which is in fact equivalent to corrosion in a weakly alkaline medium, on account of the magnesium corrosion products) the stability in time of the microcathode action will differ considerably as compared with magnesium dissolving in an acid medium. In acid solutions the microcathodes keep effective for much longer; in neutral or alkaline

media the efficacy of the cathodes decreases rather rapidly in time, through the blocking of their surfaces by magnesium corrosion products.

It is worth noting that in the corrosion of magnesium in neutral or alkaline solutions the cathodic components which enter into the composition of a metallic alloy and are not deposited on the surface, as in our case, will keep their efficiency to a greater degree. This follows, for instance, from comparison of the corrosion rates for technological and pure magnesium (Fig. 4). In this case a sealing off and blocking of microcathodes will also occur, and therefore in principle the efficacy of the cathodes will be lower when the corrosion takes place in acid solutions. But if the microcathodes are a structural component of a metallic alloy (and not deposited on the surface) then instead of cathodes separating from the surface there will be, in the corrosion zone (the surface inside the corrosion pit) new active microcathodes continually appearing in the corrosion zone, issuing from the alloy structure, as the corrosion process moves forward.

Evidently each density of current will have corresponding to it a certain quantity of actively operating cathodes, because of an equilibrium between the rate of uncovering of new cathodes and the rate of removal or sealing off of old microcathodes.

Thus greater current density means a greater quantity of active cathodes.

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Discussion of the Results

1) We have established that in the corrosion of magnesium or its alloys in a neutral NaCl solution, the pH of the solution is rapidly displaced to the alkaline side, becoming steady at pH 10.2, close to the value 10.34, which is the pH calculated from the equilibrium constant of the reaction -



The slight departure of the pH from the theoretical value may, on the basis of experiments carried out, be explained by the neutralizing action of atmospheric carbon dioxide.

We have expressed the opinion that it would be expedient to carry out electrochemical experiments not in neutral chloride solutions, as is the accepted procedure, but in chloride solutions previously buffered to constant pH by the corrosion products of the metal being studied.

2) We have studied the corrosion of technological and pure magnesium, and also that of magnesium alloys ML-4 and ML-5, in an 0.5% NaCl solution. For technological magnesium, an initially somewhat reduced corrosion rate was found to be characteristic (the incubation period), followed by a gradual acceleration due to the effect of cathodic admixtures accumulating on the surface. For the ML-4 and ML-5 alloys, on the other hand, a somewhat greater corrosion in the initial period was found to be

characteristic, with a certain decrease of the corrosion rate in time, due, apparently, to the gradual formation of more of the protective film.

TABLE 5

Steady Corrosion Rates and Potentials of Magnesium and its Alloys, in
0.5% NaCl Solution Previously Buffered to pH 10.20 with Mg Corrosion Products.

<u>Metal or alloy</u>	<u>Corrosion rate (number of ml of hydrogen liberated per cm² of test-piece surface per hour)</u>	<u>Final steady potential with respect to 1 n. hydrogen electrode (V)</u>
Pure magnesium	0.085	-1.307
Technological magnesium	0.2	-1.320
ML-4 alloy	0.0114	-1.248
ML-5 alloy	0.024	-1.268
ML-4 alloy, oxidized	0.006	-1.240

It is characteristic that pure magnesium has a considerably lower steady corrosion rate than technological magnesium. But the ML-4 and ML-5 magnesium alloys also show themselves much more resistant than technological magnesium.

The measured electrode potentials of the alloys in a 0.5% NaCl solution show, after a few hours, characteristic steady values. Alloys which are more corrosion-resistant as compared with technological magnesium correspond, in general, to more positive electrode potentials, and the more resistant alloys (ML-5 and especially ML-4) in the oxidized state do indeed exhibit a less negative potential.

This behavior must be connected with an increasing inhibition of the anode process as we go from technological magnesium to ML-5 alloy and then to ML-4 alloy and oxidized ML-4. Anodic inhibition, as is well known, will displace the potential of a corrosion-system to the positive side and simultaneously reduce the corrosion rate [5, 20-22].

However, in the transition from technological magnesium to pure magnesium the stable electrode potential becomes more negative, while simultaneously the corrosion rate decreases. Thus, undoubtedly, is connected with the basic increase in the cathodic inhibition of the corrosion process as we go toward pure magnesium (due to the small quantity of cathodic inclusions). It is well known that a predominant increase of cathodic inhibitions [5, 10, 14 and 15] will cause a decrease of corrosion with simultaneous displacement of the total measured potential of the corrosion system toward more negative values.

3) Study of the effect of anode polarization on the corrosion of a magnesium electrode has shown that the pure corrosion, that is, the autolysis rate of the electrode (after deduction of the purely anodic dissolution corresponding to the current passed), considerably increases with increase in the anode current density. Thus, for instance, the autolysis rate of technological magnesium, at the maximum investigated current density of mA/cm^2 , amounts to $16.8 \frac{\text{ml}}{\text{cm}^2 \cdot \text{hr}}$ (by hydrogen). If we compare this figure with the amount of pure corrosion for magnesium under the same conditions but without any applied current, namely $0.022 \frac{\text{ml}}{\text{cm}^2 \cdot \text{hr}}$, then it is obvious that at an anode current density of 50 mA/cm^2 , the amount of pure corrosion has increased 764 times.

Over the wide range of current densities investigated (from 0.5 to 50 mA/cm^2), excluding small currents commensurable with the corrosion current, the autolysis rate is nicely proportional to the anode current density (Fig. 10). In this region of current densities we have, for technological magnesium under the conditions investigated, a constant ratio of 0.82 (82%) between the autolysis current and the externally applied anode current. Thus for each 100 parts of magnesium dissolved by the anode current, a further 82 parts of magnesium are dissolved by the process of autolysis (the negative difference effect). If we compare the amount of autolysis for aluminum in approximately the same current density interval, an amount which, according to the research findings of N.D. Tomashov and V.N. Modestova [12], is 13.5% of the amount of anode dissolution, then we have to conclude that the amount of autolysis (the amount of the negative difference effect) for magnesium considerably exceeds the amount for aluminum. Consequently the amount of useless dissolving of a magnesium protective electrode or magnesium battery anode will be much higher than in the case of aluminum, unless special steps are taken to eliminate this phenomenon. From this it follows that in contacts magnesium and, it seems, magnesium alloys, will suffer from corrosion much more than aluminum and aluminum alloys, even with identical external currents in the contact circuit.

The mechanism of the proportionality established between magnesium autolysis and anode current density, or (as we may look at it if we wish) the proportionality between autolysis and the amount of anode current passed through the test-piece, cannot yet be regarded as definitely explained.

To account for this phenomenon (the negative difference effect), both chemical and electrochemical mechanisms may be invoked. In both cases the increase of autolysis is referred to a proportional increase in the active surface of the electrode by the anode current's destroying the protective film, with a subsequent acceleration of the chemical interaction between the active surface and water (in the chemical view) or an increase in the activity of new microcathodes on areas of the electrode surface stripped of protective film by the action of the anode current. In the electrochemical view of the negative difference effect, a view which seems to us the more probable, we may suppose, in the same way as has been established by Tomashov and Modestova [12] in the case of the negative difference effect on aluminum, that the microcathodes are constituted not only by micro-inclusions

in the alloy, but also to a great extent by areas of the metal itself (in this case magnesium) adjacent to the dissolving crystallographic face (the anode) and which migrate with the migration of the anode face in the solution process.

Support for this thesis may be found in the fact that even pure magnesium exhibits the phenomenon of accelerated autolysis under conditions of anode polarization in chloride solutions. Consequently there are grounds for believing that processes of magnesium autolysis occur even in the absence of foreign inclusions and [that they involve] an independent, purer cathodic phase [of the magnesium].

Thus in the electrochemical view of the negative difference effect (acceleration of autolysis with increase of anode current) we have to believe that the cathodic areas may be areas of the magnesium itself, areas having the thinnest protective film. Areas becoming thus cathodic are, it seems, parts of the magnesium surface directly adjacent to the active anode areas as the latter advance in the solution process (Fig. 17).

With this mechanism, the amount of the active cathodic surface is proportional to the amount of active anodic surface (or, if this is constant, to the rate of movement of the latter over the surface of the electrode through the dissolving of magnesium).

Since the area of the active anode surface (or the rate of its displacement) is proportional to the anode current, we can understand that the cathode efficiency also will be directly proportional to the density of the applied current. This fact will indeed guarantee a linear relationship between the autolysis rate (rate of hydrogen liberation over the magnesium anode) and the current density.

The amount of active cathodic surface is in dynamic equilibrium with the amount of active anodic surface, or, what amounts to the same thing, with the anode current density. When the anode current density is increased, the active anode surface, and the active cathode surface which depends on it, will increase in amount; when the current density is decreased, the area of active anode and cathode surface decreases proportionately.

This is well supported by the experiments which have demonstrated the reversible increase (or decrease) in the autolysis rate with increase (or decrease) in the anode current density. We may suppose that when the anode current is decreased the active anodic and cathodic surfaces are reversibly diminished; they are healed over by the passivizing action (formation of protective film) of the oxygen dissolved in the electrolyte, or even directly by the oxygen of the water.

Study of the distribution of local corrosion under conditions of anode polarization gives grounds for the statement that not all the surface within the corrosion pit is simultaneously active anodic surface. The cavity of the corrosion pit is nothing more than a place where the active anodic surface (the dissolving crystallographic face) can advance, in the course of its dissolving. The more solid protective film on the rest of the surface does not, under the constant conditions of the experiment, permit the

dissolving active face to emerge onto the surface, and thus the dissolving process is localized inside the corrosion cavity.

Conclusions

1) When magnesium corrodes in a neutral, atmospherically aerated, 0.5% NaCl solution, the solution pH moves toward the stable value 10.2.

2) It is expedient to carry out researches on electrochemical corrosion in chloride solutions previously buffered to constant pH with corrosion products of the metal under investigation.

3) The corrosion of magnesium in an 0.5% NaCl solution proceeds, after a certain incubation period, almost linearly in time.

4) The metals investigated may be arranged in the following series, according to the decline of the corrosion rate which they exhibit in an 0.5%-m NaCl solution: technological magnesium - ML-5 alloy - ML-4 alloy - pure magnesium.

5) The electrode potentials of the metals investigated show, in a 0.5%-m NaCl solution, at first a certain improvement, tending, however, toward a stable value. According to the value of the negative potential, the metals studied may be arranged in the following series: technological magnesium - pure magnesium - ML-5 alloy - ML-4 alloy - oxidized ML-4 alloy.

6) The autolysis rate of magnesium, for all anode current densities studied (from 0.2 to 50 mA/cm²), stays proportional to time, throughout all the intervals investigated (up to 17 hours).

7) The rate of magnesium autolysis increases in a linear ratio with the increase of anode current density. For 0.5% NaCl solution, the ratio of autolysis current to externally applied anode current is constant, and equal to 0.82 in the case of technological magnesium.

8) The increase of magnesium autolysis with increase of anode current may be explained by destruction of the protective oxide film on the magnesium, through facilitation of the process of chlorine ion penetration into the film, or adsorption of chlorine ion on the film, when the electrode potential is displaced to the positive side by increase of the anode current density.

9) When the anode current is decreased or cut off, the autolysis of magnesium decreases; consequently there is a reversible "healing" of the active surface areas through passivation of the magnesium by the reaction of the metal with water.

10) Upon increase of the anode current, the number of corrosion centers (pits) on the magnesium anode increases. For current densities which are not too high, the number of corrosion centers increase proportionately to the logarithm of the current density.

11) The number of corrosion centers which develop in the first instant when the current is applied to the magnesium anode remains constant in time, so long as the current density does not change.

12) For anode densities which are not too high, the general configuration of the corrosion pit is close to hemispherical. At higher current densities there appears a greater tendency for the corrosion pit to grow in width (transition to a more uniform corrosion of the electrode).

13) The true anodic surface of the magnesium electrode, the surface which is in process of dissolving at the given moment, is, we suggest, proportional to the current density and is independent of increase in the total surface area of the corrosion pit.

14) The autolysis rate for magnesium is proportional, we suggest, to the area of the true active anodic surface.

15) The principal active microcathodic surface of anodically dissolving magnesium is the surface of the magnesium itself, in areas covered by a thinner passive film. These areas are directly adjacent to the active anodic areas, moving with them as they are displaced by dissolving.

16) Under conditions of corrosion in neutral (alkaline) NaCl solutions, the efficacy of cathodes (Cu) artificially implanted on the magnesium surface diminishes rapidly with time, mainly through their being covered over by magnesium hydroxide.

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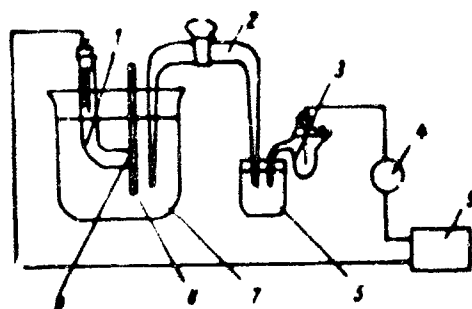


Fig. 1. Measurement of pH with glass electrode. 1 - Glass electrode. 2 - Connecting siphon. 3 - Calomel half-cell. 4 - Weston cell. 5 - Vacuum tube potentiometer. 6 - Intermediate vessel. 7 - Electrolyte, 0.5% NaCl. 8 - Magnesium test-piece. 9 - Membrane.

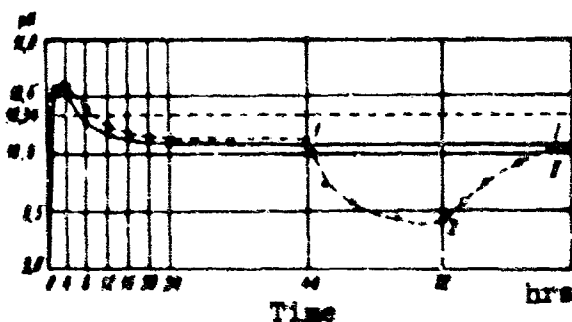


Fig. 2. Variation of pH in 0.5% NaCl solution in presence of corroding magnesium.

- I. Without removal of test-piece from solution.
- II. Test-piece removed from solution after 18 hours (1) and then re-immersed (2).

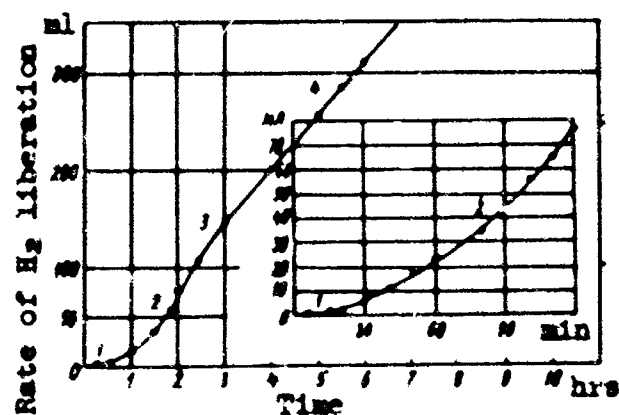


Fig. 3. Time-variation of corrosion of technological magnesium in non-buffered 0.5% NaCl solution (according to hydrogen liberated)

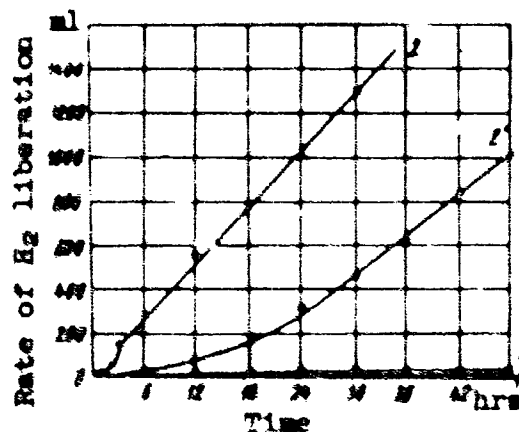


Fig. 4. Time-variation of corrosion of pure and technological magnesium over a period of 48 hours (according to hydrogen liberated).

Pure magnesium: 1 - in 0.5% NaCl solution. 1' - in 0.5% NaCl solution buffered to pH 10.2.
Technological magnesium: 2 - in 0.5% NaCl solution. 2' - in 0.5% NaCl buffered to pH 10.2.

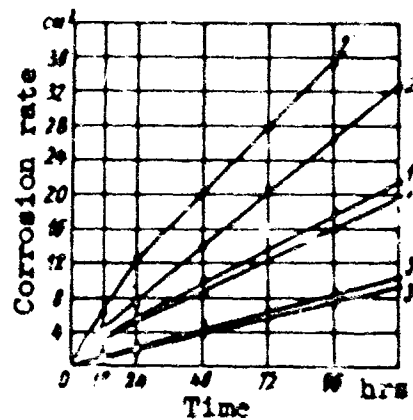


Fig. 5. Variation of corrosion of ML-4 and ML-5 alloys, over a period of 5 days.

ML-4 alloy: 1 - in 5% NaCl solution: 1' in 0.5% NaCl solution buffered to pH 10.2.
ML-5 alloy: 2 - in 5% NaCl solution: 2' - in 5% NaCl solution buffered to pH 10.2.
ML-4 alloy, oxidized: 3 - 0.5% NaCl solution: 3' - in 0.5% NaCl buffered to pH 10.2

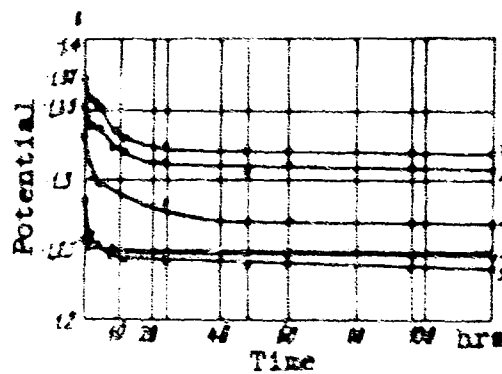


Fig. 6. Time-variation of potential in 0.5% NaCl solution.

1 - Pure magnesium: 2 - Technological magnesium: 3 - ML-4 alloy: 4 - ML-5 alloy: 5 - ML-4 alloy, oxidized

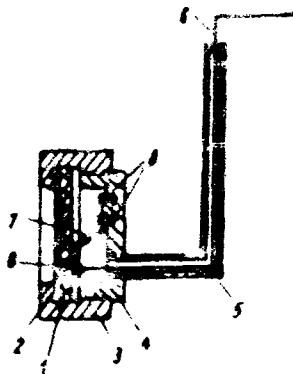


Fig. 7. Mounting of test-piece in plexiglass holder.

- 1 - Test piece, magnesium disc.
- 2 - Rubber seal.
- 3 - Screw cap of plexiglass holder.
- 4 - Base of plexiglass holder.
- 5 - Plexiglass tube.
- 6 - Copper lead-wire.
- 7 - Brass spring contact.
- 8 - Lead-wire soldered to contact.
- 9 - Screws securing contact-spring to plexiglass holder.

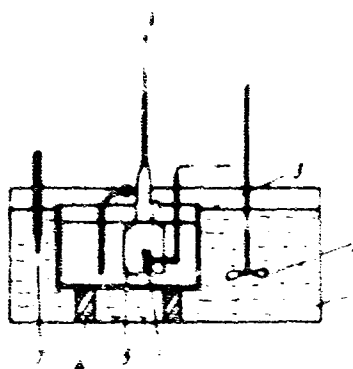


Fig. 8. General view of apparatus for determining magnesium corrosion rate.

- 1 - Thermostat.
- 2 - Mixer.
- 3 - Tank.
- 4 - Support.
- 5 - Burette for collecting hydrogen.
- 6 - Magnesium test-piece.
- 7 - Thermometer.

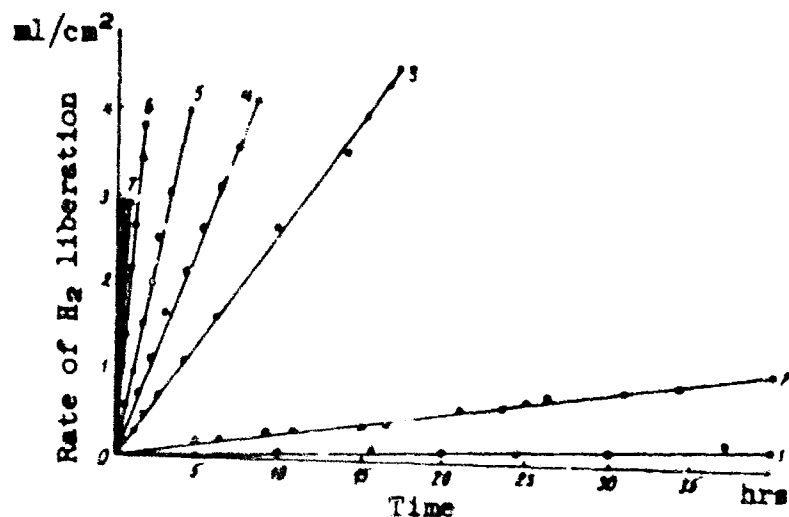


Fig. 9. Time-variation of autolysis rate of magnesium electrode for different anode current densities.

Current density (mA/cm^2): 1 - 0; 2 - 0.2; 3 - 0.5; 4 - 1; 5 - 2; 6 - 10; 7 - 20; 8 - 50.

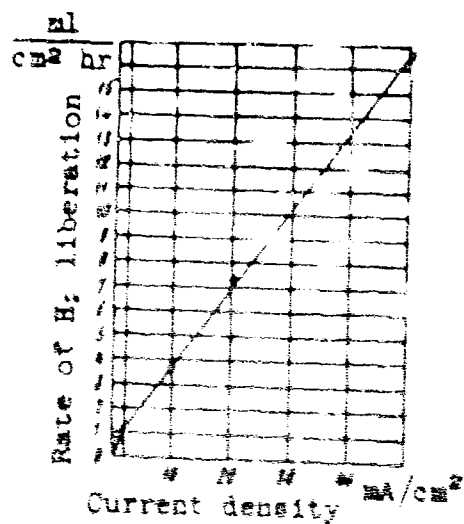


Fig. 10. Variations of autolysis rate, magnesium electrode, in relation to current density.

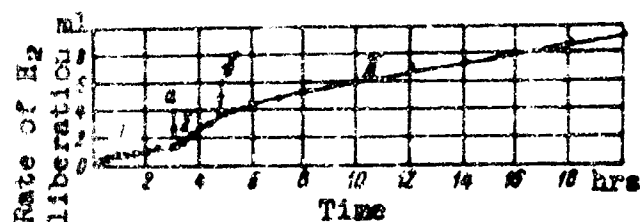


Fig. 11. Time-variation of autolysis process, magnesium electrode, with application and removal of anode current.

- a) Anode current 0.5 mA/cm^2
- b) Current switched off.

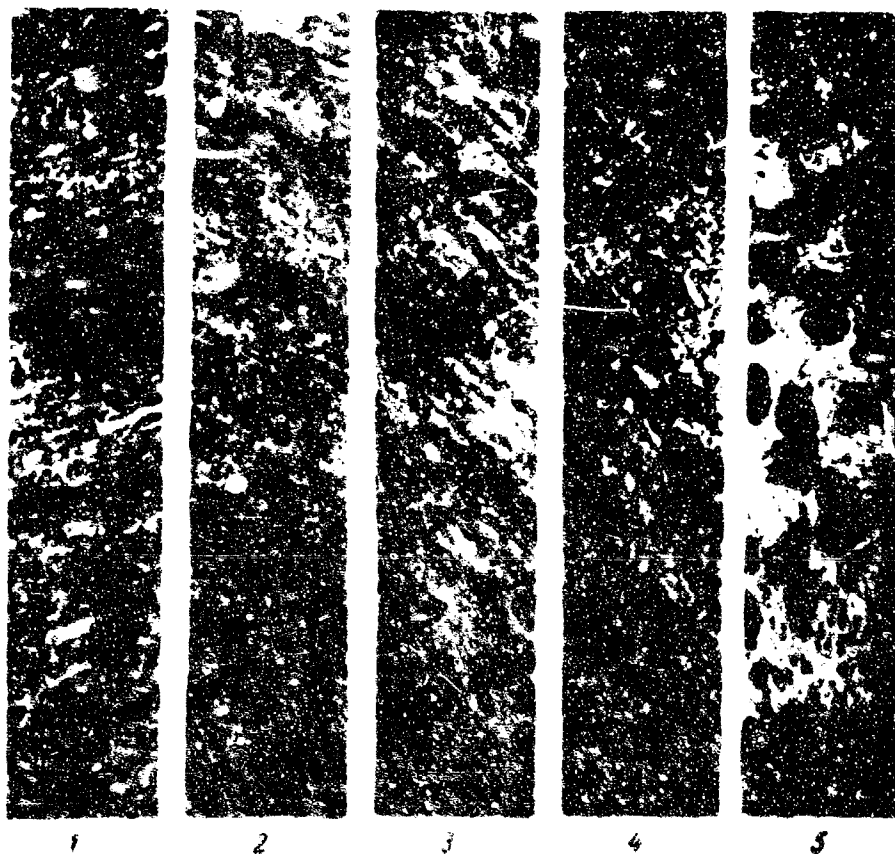


Fig. 12. Character of local corrosion on technological magnesium (growth of corrosion cavities) with passage of time; polarization, anode current of 0.5 mA/cm^2 . Magnified 15 times.

Duration of polarization of test-pieces (hours):
 1 - 2; 2 - 4; 3 - 6.5; 4 - 9; 5 - 13.5.

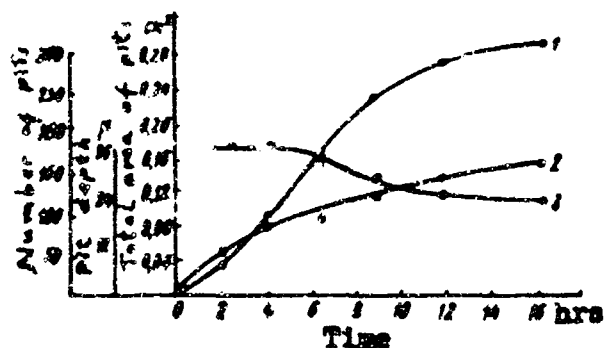


Fig. 13. Growth of corrosion pits in time, at constant current density 0.5 mA/cm^2 .

1 - Area of pits on surface;
2 - Corrosion-pit depth; 3 - Number of corrosion pits.

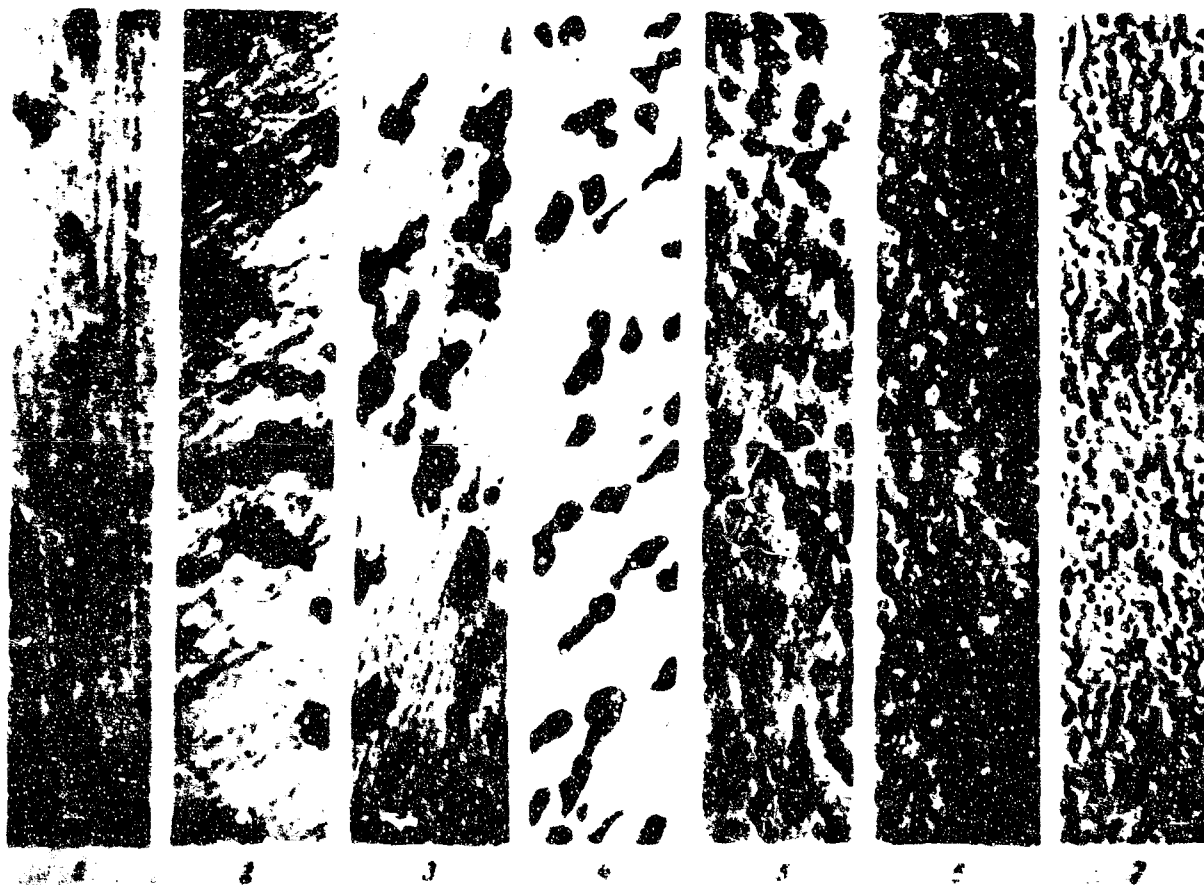


Fig. 14. Surface appearance of magnesium test-pieces after anodic polarization with currents of various densities, but with equal quantities of electricity transmitted.

Current density (mA/cm^2): 1 - 0.1; 2 - 0.2; 3 - 0.5;
4 - 1; 5 - 2; 6 - 10; 7 - 50.

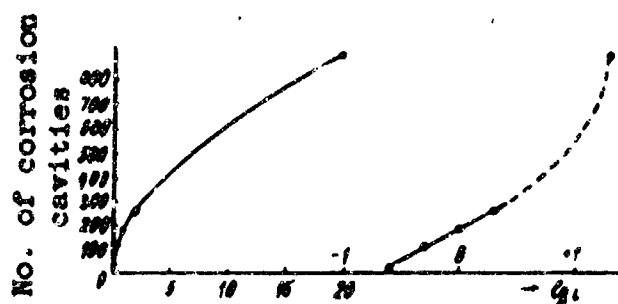


Fig. 15. Relation between number of corrosion centers and anode current density.

a - Simple plot; b - Semi-logarithmic plot.

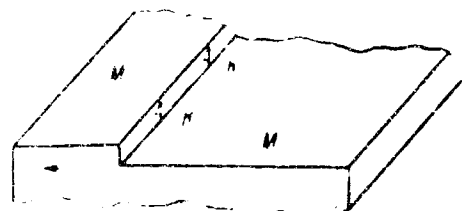


Fig. 17. Diagram of anodic dissolving of magnesium.

AA - Dissolving face (anode surface), displaced as it dissolves, as indicated by the arrow; KK - Zone adjacent to anode surface has thinner passive film than remaining surface (M), and plays the part of the basic cathode.

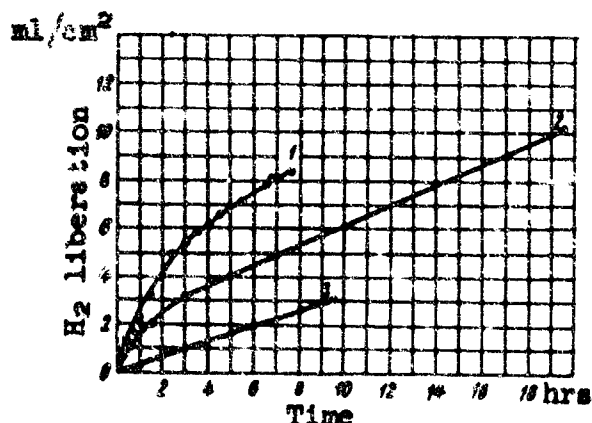


Fig. 16. Time dependence of autolysis process with anode polarization, for magnesium electrodes with different amounts of cathodic components. Current density 0.5 mA/cm^2 .

1 - Magnesium electrode plated with copper for one minute. 2 - Magnesium electrode plated with copper for twenty seconds. 3 - Magnesium electrode without copper deposit.